

Actinide—3*d*-metal Laves-phase intermetallic compounds: Magnetism and electronic properties

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The magnetic properties of actinide—3*d*-metal Laves-phase compounds $\mathcal{A}Fe_2$, $\mathcal{A}Co_2$, and $\mathcal{A}Ni_2$ ($\mathcal{A}=U, Np, Pu$) are qualitatively discussed. The adopted model uses a tight-binding description of the one-electron states and *d-f* hybridization. The electron-electron interactions are described on the basis of the Hartree-Fock model. The general, wave-vector-dependent, magnetic response for this coupled and hybridized system is obtained and a magnetic instability criterion is derived. Isostructural compounds of stable rare-earth elements are compared with these actinide systems. The changes in the magnetic properties due to alloying and off-stoichiometry effects are briefly discussed. A close similarity between Laves-phase cerium and actinide compounds is exhibited.

The electronic structure and magnetic properties of Laves-phase rare-earth (\mathcal{L}) intermetallic compounds have been extensively studied;¹ on the contrary, actinide (\mathcal{A}) Laves-phase compounds have received less attention from the theoretical point of view. Recent band calculations are available for the electronic structure of some Laves-phase compounds² (general form AB_2), for $B=Mn, Fe, Co, Ni$, and $A=Y, Zr$. When A is a stable rare-earth element, the magnetic properties of the corresponding compounds have been classified into three main groups: (i) self-sustained 3*d*-band magnetism, with *d* states being coupled to the localized 4*f* moments, e.g., $GdFe_2$ (Ref. 1); (ii) 4*f*-spin-induced local magnetic moments in a *d*-like band, e.g., $Gd(Ir_{1-x}Co_x)_2$;³ and (iii) Ruderman-Kittel-Kasuya-Yosida (RKKY) like ordering through the *s-d* band electrons, e.g., $GdNi_2$.¹

Recent systematic experimental studies concerning actinide—transition-metal Laves-phase compounds AB_2 (Refs. 4–7) exhibit quite peculiar magnetic and structural properties. These studies involve U, Np, and Pu compounds with Fe, Co, and Ni, pseudobinary compounds $A(B_{1-x}B'_x)_2$, and nonstoichiometry effects. These studies^{4–7} raise the following questions, among others.

(i) How can one compare the magnetic properties of isostructural rare-earth compounds with the corresponding actinide ones? Equivalently, how should one modify the models for the rare-earth compounds to include the effect of larger spatial extension of the 5*f* shells?

(ii) How does alloying these 5*f* compounds with transition or noble metals compare with the corresponding 4*f* ones?

Before describing the theoretical model we suggest for these systems, let us briefly mention the observed distances R_{ff} between 5*f* elements in compounds AB_2 .⁴ Actinide compounds of U, Np, and Pu with Fe and Co show decreasing R_{ff} values when one passes from Fe to Co. On the contrary, in passing from Co to Ni, R_{ff} increases,⁴ attaining values comparable to those observed in actinide compounds with Fe. This behavior is shown schematically in Fig. 1, together with the observed trend

for the case of stable rare-earth compounds (e.g., Gd and Lu). The case of actinide compounds with Ni is anomalous and may be considered as one of the first indications of deviations associated with the 5*f*-shell extension.

Let us begin the formulation of the model we adopt for these 5*f* intermetallic compounds by defining the approximations used for the electronic states. The 5*f* and *d*-like bands are described within the tight-binding approxima-

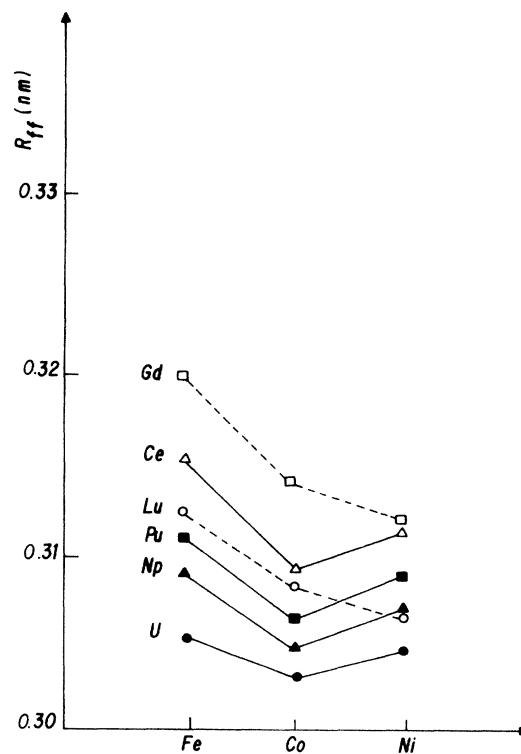


FIG. 1. Interatomic 4*f* and 5*f* distances (R_{ff}) of various $\mathcal{A}B_2$ and $\mathcal{L}B_2$ Laves-phase compounds ($\mathcal{A}=U, Np, Pu$; $\mathcal{L}=Ce, Gd, Lu$; $B=Fe, Co, Ni$) collected from Refs. 4 and 10.

tion. Consistently, the $5f$ band originates from the overlap between neighboring $5f$ shells. As shown in Fig. 2 of Ref. 8, a clear distinction occurs between light actinides and \mathcal{L} metals regarding the spatial extension of the f states. This is a very relevant point since the extreme localization of f electrons, so characteristic of rare-earth metals, is not reached even in the limiting situation of heavy actinides like Bk.⁸ In Fig. 2 of Ref. 8, one sees that the radial extension decreases in passing from U to Pu; a sharp decrease occurs in going to Am and one attains the limiting case of Bk. The results in Fig. 2 of Ref. 8 are obtained from very sophisticated band calculations. We use the connection between resonant phase shifts and tight-binding parameters to say qualitatively that the $5f$ -band width is expected to⁹ decrease in passing from U to Np and Pu. This behavior is connected with both the increasing R_{ff} distances (see Fig. 1) and the decreasing spread of the $5f$ orbitals when going from U to Pu. The second effect is just a measure of the stabilization (and consequently, increased localization) of the $5f$ orbitals along the actinide series. The first one is in fact a self-consistent effect: changes in local band structure imply changes in occupation number at sites A and B via charge transfer.¹⁰ Thus the lattice parameters increase to an equilibrium value controlled by these transfers and by elastic forces.¹⁰ Independently of a detailed discussion of the first effect, both contributions tend to reduce the $5f$ -band width.

The same effect of narrowing of the associated local band is expected with the $3d$ orbital stabilization in going from Fe to Ni. As for the band originating from the very extended actinide $6d$ states, one expects it to be a very broad band and to have a small density of states; therefore we completely disregard the $6d$ band. We also do not consider the s - p states which are very relevant in discussing both hyperfine data and transport properties; thus we restrict our discussion to the properties mainly associated with $5f$ and $3d$ states. In the above described one-electron hoppings, we considered only f -electron hopping between A sites and d -electron hoppings among B sites.

We include also the possibility of d - f hybridization, as usual in the description of pure actinide metals.^{8,11} In Fig. 2 of Ref. 8, to illustrate the argument in favor of delocalization versus hybridization, the spatial extension of the $3d$ wave function in pure Fe is shown to be comparable with the corresponding extension for actinides. Let us assume a tight-binding description of d - f hybridization.¹¹ This involves the strengths of d - f overlaps, and one expects to have decreasing hybridization with increasing localization of f or d states (at constant lattice spacing).

Formally, the one-electron states for these intermetallic compounds must be derived from a matrix involving $f \times f$, $d \times d$ blocks, together with $d \times f$ and $f \times d$ hybridization blocks. In this work, however, we adopt a simple model for the one-electron states. We start from homothetic bands $\epsilon_{\mathbf{k}}^{(d)}$ and $\epsilon_{\mathbf{k}}^{(f)}$ defined by

$$\epsilon_{\mathbf{k}}^{(f)} = \gamma \epsilon_{\mathbf{k}}^{(d)} + \delta. \quad (1)$$

In $\epsilon_{\mathbf{k}}^{(d)}$ we include electron hoppings between B sites, together with processes where a d -electron hops from one B site to another through states other than the $3d$ or $5f$

ones. In $\epsilon_{\mathbf{k}}^{(f)}$ the γ factor ($\gamma \ll 1$) describes the effect of the smaller overlap between $5f$ atoms (located in A sites at distance R_{ff}). We also include in γ , the corrections due to hoppings associated to mixing with non- d or non- f states. As mentioned in Ref. 8, the Hill plot argument is not the only control for itinerancy of the $5f$ states. The f -electron delocalization is also influenced by s - f and p - f hybridization. These effects are phenomenologically included in γ . The parameter γ , together with the d -band width will play a central role in our picture. The center of the $5f$ band with respect to the $3d$ band is specified by δ . Finally, d - f hybridization may be taken for simplicity as a \mathbf{k} -independent phenomenological parameter $|V_{df}|$. Varying the strength of the parameter $|V_{df}|$, we simulate the effects of changing d - f overlaps associated with the spatial extension of either the $5f$ or $3d$ wave functions. In order to describe the magnetic properties, we introduce the electron-electron interactions U_{ff} , U_{dd} , and U_{df} . Due to the spatial extension of d and f wave functions, one has

$$U_{ff} > U_{df} > U_{dd}. \quad (2)$$

The one-electron Hamiltonian associated with Eq. (1), d - f hybridization, and the electron-electron interactions mentioned above, define the model for these actinide intermetallic compounds.

It is interesting to review the case of stable rare-earth intermetallic compounds starting from the above picture. First of all, let γ tend to zero ($\gamma \rightarrow 0$) and at the same time $|V_{df}| \rightarrow 0$. The last requirement reflects only the almost-vanishing probability of d - f hopping, whereas the first reflects rather localized f states. The rare-earth magnetic moment in this simple model is mainly associated with the U_{ff} interaction. Since degeneracy is completely absent here, Coulomb and exchange interactions between different f orbitals are not taken into account. Thus we only mimic Hund's rule through U_{ff} . The exchange interaction between the rare-earth moment and the d states follows from a U_{df} -type interaction (see Ref. 12). Finally, the existence of U_{dd} is at the origin of the above-mentioned d -band sustained magnetism (e.g., GdFe^2), or rare-earth-induced d magnetic moments [e.g., $\text{Gd}(\text{Ir}_{1-x}\text{Co}_x)_2$].

Let us briefly recall some theoretical results² obtained for transition-metal intermetallic compounds YB_2 with $B = \text{Fe}, \text{Co}, \text{Ni}$. These results will be useful later on for the qualitative discussion of the corresponding actinide compounds. The tight-binding calculations² show a local $3d$ density of states whose width decreases in passing from Fe to Ni. This agrees with the decreasing extension of the $3d$ orbitals. We argue that the same should occur for a given actinide and with variation of the transition-metal partner. Another important point following from Ref. 2 concerns the total d density of states. The low-energy part of the band is dominated by the $3d$ local density of states, with $4d$ states arising from Y atoms lying mostly in the high-energy part. In the case of YNi_2 , from Ref. 2 we see that the position of the Fermi level is such that the $3d$ density of states is small enough to inhibit ferromagnetism. Clearly the same occurs for the broader $4d$ band.

The question now is how to treat correlations in the case where $\gamma \neq 0$ and $|V_{df}| \neq 0$. For a given band width Δ for the d electrons, from Eq. (1) one has the f -band width $\Delta_f = \gamma\Delta$. Since for $3d$ states one expects $U_{dd}/\Delta < 1$, it seems reasonable to treat the d - d electron correlations within the Hartree-Fock (HF) approximation. Similarly, one expects $U_{df}/\Delta < 1$ and again the HF scheme seems suitable. It remains only to specify the treatment of electron correlations among f electrons. The adequate approximation depends on the ratio $U_{ff}/\gamma\Delta$;

thus γ controls the strength of f - f correlations. Two limiting situations may be considered: (i) the Hartree-Fock approximation for f - f , d - f , and d - d correlations, or (ii) the Hubbard approximation for f - f correlations in the presence of HF-like d - d and d - f correlations.

In this work we quote only the results obtained within the Hartree-Fock scheme,^{13,14} reserving the strong-correlation limit for a separate publication.¹⁵ The wave-vector-dependent, static magnetic susceptibility for this coupled, hybridized system of d - f electrons is

$$\chi_{\alpha}^{\text{HF}}(\mathbf{q}) = \frac{\tilde{\chi}_{\alpha}(\mathbf{q}) + U_{\beta\beta}^{\text{eff}}(\mathbf{q})\tilde{\chi}_{\alpha}(\mathbf{q})\chi_{\beta}(\mathbf{q}) - U_{df}^{(\alpha)}(\mathbf{q})\chi_{\alpha}(\mathbf{q})\tilde{\chi}_{\beta}(\mathbf{q})}{[1 - U_{dd}^{\text{eff}}(\mathbf{q})\chi_d(\mathbf{q})][1 - U_{ff}^{\text{eff}}(\mathbf{q})\chi_f(\mathbf{q})] - U_{df}^{(d)}(\mathbf{q})U_{df}^{(f)}(\mathbf{q})\chi_d(\mathbf{q})\chi_f(\mathbf{q})}, \quad \alpha, \beta = d, f, \quad \alpha \neq \beta, \quad (3)$$

where the effective electron-electron interactions are defined by

$$U_{\alpha\alpha}^{\text{eff}}(\mathbf{q}) = U_{\alpha\alpha} \left[1 + \frac{U_{df}}{U_{\alpha\alpha}} \frac{\chi_{\alpha}^{\text{mix}}(\mathbf{q})}{\chi_{\alpha}(\mathbf{q})} \right], \quad (4a)$$

$$U_{df}^{(\alpha)}(\mathbf{q}) = U_{df} \left[1 + \frac{U_{\beta\beta}}{U_{df}} \frac{\chi_{\alpha}^{\text{mix}}(\mathbf{q})}{\chi_{\alpha}(\mathbf{q})} \right], \quad \alpha = d, f, \quad \alpha \neq \beta. \quad (4b)$$

The magnetic susceptibilities in the absence of interactions which appear in Eqs. (3) and (4) are defined as follows:

$$\chi_{\alpha}^{\text{mix}}(\mathbf{q}) = \sum_{\mathbf{k}} V_{\alpha\beta}(\mathbf{k} + \mathbf{q}) V_{\beta\alpha}(\mathbf{k}) \chi_{\text{mix}}(\mathbf{k}, \mathbf{q}), \quad (5a)$$

$$\tilde{\chi}_{\alpha}(\mathbf{q}) = \chi_{\alpha}(\mathbf{q}) + \chi_{\alpha}^{\text{mix}}(\mathbf{q}), \quad (5b)$$

$$\chi_{\alpha}(\mathbf{q}) = \sum_{\mathbf{k}} \sum_{\mu, \nu=1}^2 (-1)^{\mu, \nu} \frac{(E_{\mathbf{k}}^{(\mu)} - E_{\mathbf{k}+\mathbf{q}}^{(\beta)})(E_{\mathbf{k}+\mathbf{q}}^{(\mu)} - E_{\mathbf{k}}^{(\beta)})f(E_{\mathbf{k}+\mathbf{q}}^{(\mu)}) - (E_{\mathbf{k}}^{(\nu)} - E_{\mathbf{k}+\mathbf{q}}^{(\beta)})(E_{\mathbf{k}}^{(\nu)} - E_{\mathbf{k}+\mathbf{q}}^{(\beta)})f(E_{\mathbf{k}}^{(\nu)})}{E_{\mathbf{k}+\mathbf{q}}^{(1)} - E_{\mathbf{k}+\mathbf{q}}^{(2)}(E_{\mathbf{k}}^{(1)} - E_{\mathbf{k}}^{(2)})(E_{\mathbf{k}+\mathbf{q}}^{(\mu)} - E_{\mathbf{k}}^{(\nu)})}, \quad (5c)$$

$$\chi_{\text{mix}}(\mathbf{q}) = \sum_{\mathbf{k}} \sum_{\mu, \nu=1}^2 \frac{f(E_{\mathbf{k}+\mathbf{q}}^{(\mu)}) - f(E_{\mathbf{k}}^{(\nu)})}{(E_{\mathbf{k}+\mathbf{q}}^{(1)} - E_{\mathbf{k}+\mathbf{q}}^{(2)})(E_{\mathbf{k}}^{(1)} - E_{\mathbf{k}}^{(2)})(E_{\mathbf{k}+\mathbf{q}}^{(\mu)} - E_{\mathbf{k}}^{(\nu)})}, \quad (5d)$$

and the energies $E_{\mathbf{k}}^{(\mu)}$ are defined as the roots of the equation:

$$(w - E_{\mathbf{k}}^{(d)})(w - E_{\mathbf{k}}^{(f)}) - |V_{df}(\mathbf{k})|^2 = 0. \quad (5e)$$

Equation (3) is the general HF, wave-vector-dependent, susceptibility including d - f hybridization and the electron-electron interactions. From Eq. (5) one sees that hybridization effects manifest implicitly through the new dispersion relations $E_{\mathbf{k}}^{(\nu)}$ [see Eq. (5e)] and explicitly in the definition of the $\chi_{\alpha}^{\text{mix}}(\mathbf{q})$ susceptibility [see Eq. (5a)]. Also, the origin of the effective, \mathbf{q} -dependent, electron-

electron interactions (4) is directly connected to d - f hybridization through $\chi_{\alpha}^{\text{mix}}(\mathbf{q})$. From Eq. (3) one sees that the f and d susceptibilities, as expected, exhibit the same poles; clearly for a given applied field, the residues will be different, and therefore different $5f$ or $3d$ magnetization will be induced. It is interesting, in view of some qualitative remarks concerning the magnetic behaviors quoted in Ref. 4 (see also Table I), to recover from Eq. (3) some limiting situations. The first case is the absence of d - f hybridization and has been already applied to the study of simple actinide metals.¹⁶ Equation (3) becomes

TABLE I. Critical temperature (T_c), magnetic moments at the \mathcal{A} and $3d$ sites ($\mu_{\mathcal{A}}$ and μ_T), and paramagnetic susceptibility (χ) of various $\mathcal{A}B_2$ Laves-phase compounds, collected from Ref. 4.

$\mathcal{A}B_2$	T_c (K)	Fe		Co	T_c (K)	Ni	
		$\mu_{\mathcal{A}}$	μ_T			$\mu_{\mathcal{A}}$	μ_T
		(μ_B)				(μ_B)	
U	162	0.03	0.6	$\chi = 10^3 \times 10^{-6}$ emu/g	21	0.06	0
Np	492	1.1	1.1	anomalous (antiferromagnetic)	32	1.2	0.3
Pu	564	0.45	1.47	$\chi = 2.3 \times 10^3 \times 10^{-6}$ emu/g	$\chi = 2.5 \times 10^3 \times 10^{-6}$ emu/g		

$$\chi_{\alpha}^{\text{HF}}(\mathbf{q}, |V_{df}|=0) = \frac{\chi_{\alpha}^{(0)}(\mathbf{q})[1 - U_{\beta\beta}\chi_{\beta}^{(0)}(\mathbf{q})] - U_{df}\chi_{\alpha}^{(0)}(\mathbf{q})\chi_{\beta}^{(0)}(\mathbf{q})}{[1 - U_{dd}\chi_{d}^{(0)}(\mathbf{q})][1 - U_{ff}\chi_{f}^{(0)}(\mathbf{q})] - U_{df}^2\chi_{d}^{(0)}(\mathbf{q})\chi_{f}^{(0)}(\mathbf{q})} \quad (6)$$

Clearly for $U_{df}=0$ one recovers the classical result for the HF susceptibilities. The most important limit for a quantitative discussion of experimental findings is the following:

$$\chi_{\alpha}^{\text{HF}}(\mathbf{q}, U_{df}=0) = \frac{\chi_{\alpha}(\mathbf{q})[1 - U_{\beta\beta}\chi_{\beta}(\mathbf{q})] - U_{\beta\beta}\chi_{\alpha}^{\text{mix}}(\mathbf{q})\chi_{\beta}(\mathbf{q})}{[1 - U_{dd}\chi_{d}(\mathbf{q})][1 - U_{ff}\chi_{f}(\mathbf{q})] - U_{dd}U_{ff}\chi_{d}^{\text{mix}}(\mathbf{q})\chi_{f}^{\text{mix}}(\mathbf{q})}, \quad \alpha, \beta = d, f, \quad \alpha \neq \beta, \quad (7)$$

since it contains d - d , f - f interactions, and hybridization effects. Before qualitatively discussing the consequences of Eq. (7), let us condense in Table I the magnetic properties of these systems, obtained in Ref. 4. In this table, for each transition metal and actinide we show the Curie temperature (only ferromagnets are considered) and magnetic moments at the A and B sites (μ_A and μ_B , respectively). In the susceptibilities $\chi_{\alpha}^{\text{HF}}(\mathbf{q})$ obtained previously we considered only the uniform case, namely, $\mathbf{q}=0$. Experimentally, only one exception is to be noted: NpCo_2 is antiferromagnetic with a Néel temperature of 15 K. We estimate that this is a pathological case, and attribute this behavior to peculiar band-structure effects. Nesting effects are expected to occur for a wave vector \mathbf{q} such that the antiferromagnetic instability is induced. In the absence of d - f hybridization and for the uniform case, it follows from Eq. (7) that the magnetic instabilities occur when

$$U_{\alpha\alpha}\rho^{(\alpha)}(E_F) = 1,$$

because

$$\lim_{\mathbf{q} \rightarrow 0} \chi_{\alpha}^{(0)}(\mathbf{q}) \sim \rho^{(\alpha)}(E_F),$$

$\rho^{(\alpha)}$ being the α density of states. Thus, in such a simplified situation three possibilities may occur.

(i) Ferromagnetic instability in the $3d$ band:

$$U_{dd}\rho^{(d)}(E_F) = 1, \quad U_{ff}\rho^{(f)}(E_F) \neq 1.$$

(ii) Ferromagnetic instability in the $5f$ band:

$$U_{dd}\rho^{(d)}(E_F) \neq 1, \quad U_{ff}\rho^{(f)}(E_F) = 1$$

(iii) Paramagnetic solution only.

Since these instabilities are obtained for $|V_{df}|=0$, we now qualitatively include hybridization effects. As mentioned above, from Eq. (7) one obtains identical poles for d - and f -electron susceptibilities. This implies that if a pole exists in Eq. (7), both d and f electrons exhibit magnetization. This result can be qualitatively understood in terms of a magnetization transfer through d - f hybridization. As an example, consider case (i) where an instability occurs in the d band. Hybridization will cause a different shift in the up- and down-spin f subbands; thus an f -band magnetization will be induced. The effect of magnetization transfer has been studied by Kishore and Joshi,¹⁷ and we intend to argue that Table I may be understood in terms of Eq. (7) (the magnetization transfer), which re-

flects different residues of Eq. (7) at the poles for $\alpha=d$ and f . We suggest the following qualitative interpretation of the results shown in Table I. Consider firstly a fixed actinide (say, U) and let us vary the transition-metal partner from Fe to Ni. As mentioned previously, the spatial extension of the $3d$ wave function tends to decrease and therefore d - f hybridization decreases. For Fe intermetallic compounds, we suggest that d - f hybridization is strong enough to inhibit $5f$ states to be magnetic [solution (i)]. Thus the d -magnetization transfers through d - f hybridization a small magnetization on the f states. Considering now different actinides with Fe, one expects (since the $5f$ wave functions contract along the actinide series),⁸ to have a decreasing d - f hybridization strength. This implies that $3d$ states, becoming less d - f hybridized, become increasingly magnetic, since the $3d$ density of states is expected to increase. The $5f$ states, on the other hand, become more polarizable, since their susceptibility tends to increase (larger f density of states), though not enough to stabilize magnetism. The acquired f magnetization through d - f magnetization transfer thus increases. This qualitatively explains the first block of Table I. In passing from Fe to Co one increases the number of $3d$ electrons, and we want to suggest that this is the dominant effect for Co intermetallic compounds. Except for the pathological case of Np intermetallic NpCo_2 , all those with Co are paramagnetic. We describe this by saying that neither the $3d$ nor the $5f$ states can satisfy the instability condition, and no magnetization transfer occurs. In passing from U to Pu, the strength of d - f hybridization again decreases. Thus, both densities of states tend to increase, and so do the Pauli susceptibilities. This is consistent with the experimental findings shown in Table I; the susceptibility of PuCo_2 is a factor 2 larger than the corresponding susceptibility of UCo_2 .

Let us now consider Ni intermetallic compounds, which present a quite different magnetic behavior as compared to Fe compounds. Two main differences are to be expected. Firstly, we assume the d band to have a structure similar to that observed in compounds like YNi_2 .² Thus the $3d$ density of states is expected to be very small at the Fermi level. This inhibits the $3d$ magnetic instability more strongly still than in Co compounds. Secondly, the $3d$ wave functions for Ni have smaller spatial extension as compared to Co and Fe; this implies that the strength of $|V_{df}|$ hybridization is the smallest along the transition series. Both effects, small $3d$ density of states and small $|V_{df}|$, suggest that only the sufficiently high $5f$ density of states can have a magnetic instability. In contrast to Fe intermetallic compounds, Ni compounds show $5f$ mag-

netization, and an almost vanishing magnetization at the 3d element site. This fact is experimentally confirmed through neutron-diffraction experiments.⁴ We have thus performed a crossover from a magnetic 3d band and induced 5f moment to a magnetic 5f band and almost non-magnetic Ni atoms. Since both hybridization effects and 3d density of states are small, passing from U to Np corresponds to filling a 5f band. Since in the simplest cases the 5f density of states is expected to increase, the 5f moments do increase and a small induced moment can appear in Ni atoms as indeed was observed. The case of PuNi₂ compound, which is paramagnetic, is anomalous; we ascribe this to an accident in the 5f density of states. This point needs careful study, eventually a measurement of the electronic specific heat.

Concerning alloying effects, a selective replacement of transition atoms *B* by other *B'* or noble metals shows results which may check the description of pure compounds. Consider the alloy systems $U(\text{Fe}_{1-x}\text{Co}_x)_2$, where $x = 0.0, 0.1, 0.2,$ and 0.3 .⁶ The 3d magnetic moment varies from $0.6\mu_B$ for the pure intermetallic, to $0.45\mu_B$ for $x = 0.1$, to $0.30\mu_B$ for $x = 0.2$, to $0.075\mu_B$ for $x = 0.3$. A simple rigid-band model, together with the previous discussion, enables us to understand this behavior by suppressing, with the increasing number of electrons, the 3d magnetic instability. The observed Curie temperatures are 162, 129, 87, and 24 K, respectively, for the corresponding Co concentrations. These alloy experiments are complemented by low-temperature specific-heat measurements performed in alloys of UNi₂, replacing Ni by Co, Fe, or Cu.⁵ A first comment concerns Fig. 2 of Ref. 5. There, the electronic specific heat γ is shown for UFe₂, UCo₂, and UNi₂, together with the alloys. Experiments are consistent with the above discussion; $\gamma(\text{UFe}_2) > \gamma(\text{UCo}_2)$, as expected from the 3d sustained magnetism of UFe₂ and the paramagnetic properties of UCo₂. For UNi₂ a γ value larger than both UFe₂ and UCo₂ is compatible with a high 5f density of states and thus with the 5f sustained magnetic order proposed for this compound. Concerning alloys of UNi₂ with Co and Fe, again a simple rigid-band model is enough to understand the increase of γ , since the Co and Fe shift the Fermi level to higher 3d density of states. Simultaneously, the *d-f* hybridization is expected to increase; magnetization should then decrease as was indeed observed.

A very peculiar situation occurs with Cu impurities in UNi₂. A Cu impurity introduces one extra electron with respect to Ni. We want to suggest that since the *d* density of states at the Fermi level is small, intra *d*-band screening of the extra charge is difficult to perform. Thus, this charge will be transferred to the 5f states. This increases simultaneously the 5f density of states and the magnetization, in agreement with γ (Ref. 5) and magnetic measurement. Let us comment on the behavior of R_{ff} in terms of the transition-metal partner. We assume as in Ref. 10, that the lattice parameter, or for this particular case, the 5f-5f distance R_{ff} is strongly influenced by the *d*-electron occupation number at the intermetallic sites *A* or *B*.¹⁰ This picture supposes the existence of a local *d* density of states at sites *B* and is hardly applicable to compounds like $\mathcal{A}\text{Al}_2$. We simply intend to argue that in passing from Mn to Fe and Co one maintains a considerable *d* character at the *B* sites. In going to Ni, the *d* character is strongly reduced and *s-p* states become very relevant in the cohesion; thus the increase in R_{ff} needs an extension of [10] to include the role of *s-p* states.

Concerning again R_{ff} distances, we have shown in Fig. 1 the corresponding values for CeFe₂, CeCo₂, and CeNi₂. There is a clear difference between these results for Ce and the corresponding ones for stable rare earths (very localized 4f orbitals), like Gd and Lu, where the R_{ff} distance always decreases when one passes from Fe to Ni. This is in perfect agreement with recent claims that Ce compounds are much more closer to actinide intermetallic compounds than their rare-earth partners, confirmed by band calculations,¹⁸ which show the existence of finite-width 4f-bands.

As a final remark, consider off-stoichiometry effects.⁷ We want to suggest a close similarity in the UNi_{2±x} compounds and the U(Ni_{1-x}Cu_x)₂ alloys.⁵ In fact, off-stoichiometry effects, namely, the increase of the magnetic moment with increasing U concentration, are ascribed to the increase of the 5f occupation number. Thus one expects a higher 5f density of states, and the increase in magnetization follows. The same effect occurs for U(Ni_{1-x}Cu_x)₂ alloys as discussed above, since the excess electron goes to the 5f states. These remarks suggest that it should be interesting to perform experiments on similar compounds and alloys with Np and Pu.

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